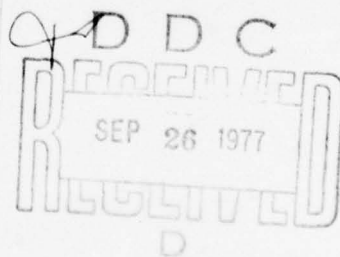END
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THE STUDY OF THE INTERACTION OF SILICON,
ITS MONOXIDES, AND DIOXIDES WITH CHLORINE

By

Yu. P. Kuznetsov, Ye. S. Petrov, A. I. Vakhrusheva

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EDITED TRANSLATION

FTD-ID(RS)I-0076-77   1 February 1977
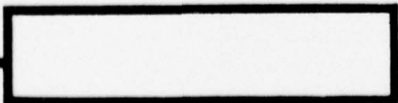
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By: Yu. P. Kuznetsov, Ye. S. Petrov, A. I.
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О о	*О о*	O, o	Ю ю	*Ю ю*	Yu, yu
П п	*П п*	P, p	Я я	*Я я*	Ya, ya

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GREEK ALPHABET

Alpha	A	α	**α**	Nu	N	ν	
Beta	B	β		Xi	Ξ	ξ	
Gamma	Γ	γ		Omicron	O	ο	
Delta	Δ	δ		Pi	Π	π	
Epsilon	E	ε	**ε**	Rho	P	ρ	**ρ**
Zeta	Z	ζ		Sigma	Σ	σ	ς
Eta	H	η		Tau	T	τ	
Theta	Θ	θ	**ϑ**	Upsilon	Υ	υ	
Iota	I	ι		Phi	Φ	φ	φ
Kappa	K	ϰ	κ	Chi	X	χ	
Lambda	Λ	λ		Psi	Ψ	ψ	
Mu	M	μ		Omega	Ω	ω	

RUSSIAN AND ENGLISH TRIGONOMETRIC FUNCTIONS

Russian	English
sin	sin
cos	cos
tg	tan
ctg	cot
sec	sec
cosec	csc
sh	sinh
ch	cosh
th	tanh
cth	coth
sch	sech
csch	csch
arc sin	$\sin^{-1}$
arc cos	$\cos^{-1}$
arc tg	$\tan^{-1}$
arc ctg	$\cot^{-1}$
arc sec	$\sec^{-1}$
arc cosec	$\csc^{-1}$
arc sh	$\sinh^{-1}$
arc ch	$\cosh^{-1}$
arc th	$\tanh^{-1}$
arc cth	$\coth^{-1}$
arc sch	sech^{-1}
arc csch	csch^{-1}

rot	curl
lg	log

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THE STUDY OF THE INTERACTION OF SILICON, ITS MONOXIDES, AND DIOXIDES
WITH CHLORINE

Yu. P. Kuznetsov, Ye. S. Petrov, A. I. Vakhrusheva

ABSTRACT

We conducted a thermodynamic calculation of the reaction of
chlorination of silicon and its oxides, on the basis of which a
conclusion was made concerning the mechanism of the occurring
interactions. We have proposed an hypothesis on the fact that
conditions of interaction of silicon monoxides with chlorine are, to
a significant degree, determined by the strength of bonds Si - O, the
weakening of which depends on both temperature and sorption of the
chlorine. The products of this interaction ($SiCl_4$ and SiO_2) were
determined.

We believe that the initial stage of the process of chlorination of silicon dioxide with chlorine in the presence of a reducer is the chemosorption of chlorine on the active sections of the surface of the oxide, which leads to a weakening of the bonds of the metals - oxygen and thereby facilitating the passing of the phase of reduction SiO_2 with carbon to the monoxide or Si, which are easily regulated with Cl_2.

We computed the apparent powers of activation for the non-isothermal conditions of reaction $Si+Cl_2$, $SiO+Cl_2$, SiO_2+C+Cl_2: 18, 39, 65 kkal/mole, respectively.

This work is a continuation of the investigation of the mechanism of chlorination of oxides of the 4A subgroup. The results for germanium and tin oxides were published in [1,2].

The probability of an occurrence of these or other interactions of silicon, its monoxides and dioxides with chlorine depending on temperature can be found by comparing the isobaric-isothermal potentials of these interactions. The importance of values ΔH and S were taken from [3,4].
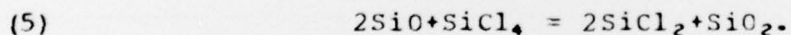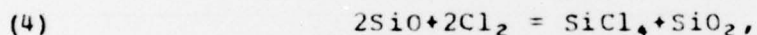
The interactions of silicon with chlorine can be described by equations

(1) $$Si + Cl_2 = SiCl_2,$$

(2) $$Si + 2Cl_2 = SiCl_4,$$
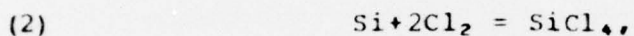
and with silicon tetrachloride - by equation

(3) $$Si + SiCl_4 = 2SiCl_2.$$
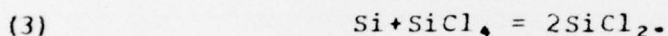
Silicon monoxide can interact with chlorine and $SiCl_4$ according to the following equations of reactions:

(4) $$2SiO + 2Cl_2 = SiCl_4 + SiO_2,$$

(5) $$2SiO + SiCl_4 = 2SiCl_2 + SiO_2.$$

At room temperature it is in a metastable state and with heating it disproportionates according to equation of reaction

(6) $$2SiO = Si + SiO_2.$$
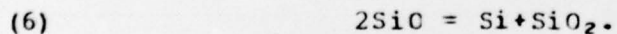
Here ΔZ has an insignificant negative value in the entire examined

temperature range. Figure 1 gives the results of the thermodynamic
calculations of some possible reactions of the process of
chlorination of SiO_2 both in the presence of a reducer and without
it.

The interaction of silicon dioxide with chlorine

(7) $$SiO_2 + 2Cl_2 = SiCl_4 + O_2$$
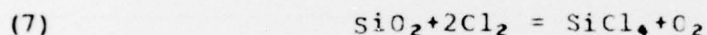
is thermodynamically improbable, consequently it can not be one of
the phases of the chlorination process. To a still greater degree
this relates to reaction

(8) $$SiO_2 + SiCl_4 = 2SiCl_2 + O_2.$$
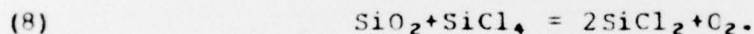
The introduction of a reducer into the examined interactions led
to a substantial shift of the isobaric-isothermal potentials of
reactions to an area of more negative values:

(9) $$SiO_2 + C + 2Cl_2 = SiCl_4 + CO_2,$$

(10) $$SiO_2 + C + Cl_2 = SiCl_2 + CO_2,$$

(11) $$SiO + 2C + 2Cl_2 = SiCl_4 + 2CO,$$

(12) $SiO_2 + C + SiCl_4 = 2SiCl_2 + CO_2.$
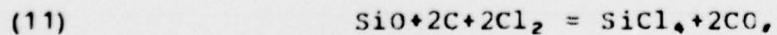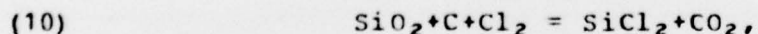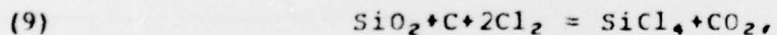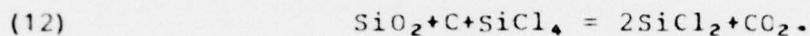
Moreover, introducing carbon into the system it makes possible the processes of reduction

(13) $SiO_2 + C = Si + CO_2,$

(14) $SiO_2 + 2C = Si + 2CO,$

(15) $2SiO_2 + C = 2SiO + CO_2.$

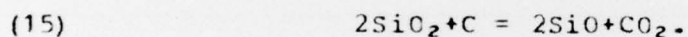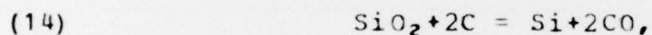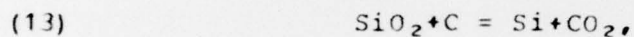Comparing the change of isobaric-isothermal potentials of the processes of reduction with the processes of chlorination of silicon dioxide with chlorine or other chloral agents we find that as a result of the sharp change of value ΔZ of the processes of reduction in comparison with chlorination without a reducer, the primary will be processes even if there is partial reduction, i.e. to SiO, on which, at last, conditions of chlorination of silicon dioxide also depends.

With the purpose of a more detailed interpretation of the question concerning the mechanism for chlorination of silicon oxides

Fig.1.

Fig.2.

Fig. 1. Change of isobaric-isothermal potential from temperature.

Key. (1) Kcal/mole

Fig. 2. Tensiogram of interactions Si+Cl$_2$ (1) , SiO+Cl$_2$ (2), SiO [vitrecus]+Cl$_2$ (3).
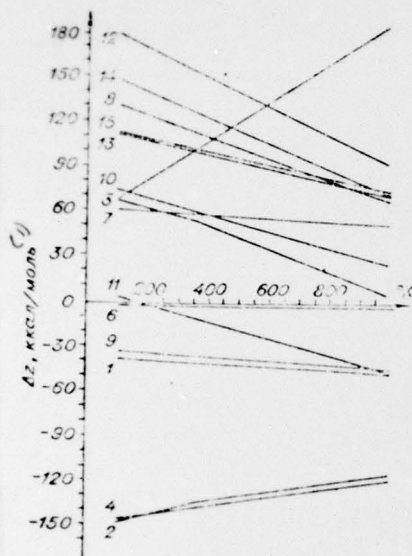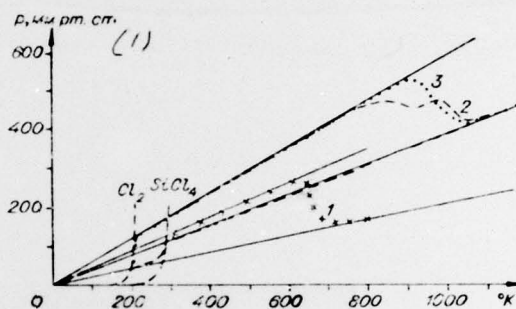
Key: (1) mm mm Hg.

with chlorine, tensimetric investigations were conducted for the
interactions $SiO + Cl_2$; $SiO_2 + Cl_2$; $Si + Cl_2$; $SiO_2 + Cl_2 + C$. The research
method did not differ from the one described earlier [1].

In the work we used chemically pure silicon, silicon monoxide,
commercial, type 4, chemically pure silicon dioxide; and spectro-pure
carbon. Chlorine was acquired by [1].

The interaction of elemental silicon with chlorine was studied
in a temperature range of 300-1000°K (fig. 2, curve 1). From the
acquired tensiogram it follows that the interaction begins from
600-650°K and passes through reaction (2). The excess silicon from
$SiCl_4$ in the studied temperature range did not interact.

The interaction of silicon monoxide with chlorine was also
studied by the tensimetric method. The temperature conditions of
disproportionation of commercial silicon monoxide were preliminarily
studied. The SiO samples were heated in a vacuum (10^{-3} mm Hg column)
for a period of an hour at different temperatures, and then a
roentgenophase analysis was conducted on the calcined samples. The
appearance of phase SiO_2 was noticed at a temperature of 1100°K,
which attests to the passing at this temperature with a larger or
smaller reaction speed of disproportionation of SiO on SiO_2 and Si.
In the atmosphere of chlorine the interaction of SiO begins from

760°K and up to the very end passes without a sharp increase in the chlorination speed. From a termperature of 950°K the reaction moves much more actively (second phase; fig. 2, curve 2).

Silicon monoxide can be acquired as a product of sublimation with the interaction of elemental silicon with its dioxide. In its makeup, this product can contain some amount of silicon which is formed with a partial decomposition of monoxide. Moreover, the sublimates acquired in condensers differ not only in external form but also in its chemical activity [5]*.

* Footnote: The authors [5] kindly presented us with three SiO products: yellow, fibrous, and vitreous.

According to the data in [5], the yellow form has in its makeup products of disproportionation of SiO, and the two others are more pure, but differ in construction. The fibrous product is considered to be the most unstable for action of the oxidant, whereas the vitreous, on the other hand, is the most stable product, and the yellow form of SiO, according to stability, is somewhere between these two. The authors [5] note that these substances are polymers, and with thermal processing there occurs a breakdown in the Si-Si bond and the free valencies can become saturated with oxygen or halogen.

The investigations which we conducted showed that the fibrous form interacts with chlorine, beginning from 695°K, the vitreous - from 880°K, and the yellow - from 680°K, but moves to the edge slowly. The products of the reaction of these interactions were SiO_2 and $SiCl_4$; however, for some as yet unknown reason the silicon monoxide does not completely enter into the reaction.

All four forms of silicon monoxide investigated by us have a completely different reaction capacity. Silicon monoxide, which we examined at the very beginning, consists of two basic products which differ, apparently, by their structure. This can also be said of the yellow form of SiO, whereas the fibrous and vitreous forms are more homogeneous. Nevertheless, in all three latter forms an insignificant amount of elemental silicon is present, which is obvious from the tensiogram, and on these there is some deviation, from the isochore, from the temperatures where chlorination of silicon began. This fact can be explained only by the disproportionation of silicon monoxide at the moment of its acquisition. Essentially, the interaction of SiO with chlorine moves by reaction (4), which by thermodynamic calculations is also the most actively favorable.

An interaction of SiO with $SiCl_4$ in the studied temperature range was not observed; from a thermodynamic point of view, this process is also improbable (see reaction (5)).

From all that has been said it follows that if
disproportionation occurs at 1100°K, and chlorination occurs at
higher temperatures, then to consider it a determining process in
chlorination of monoxide is insufficiently true. The mechanism of
chlorination is explained, apparently, by a weakening of the strength
of the bond in molecules of silicon monoxide because of both the
sorbing chlorine and because of heating. The weakened Si-O bond
breaks, and the freed oxygen migrates to the other SiO molecule and
oxidizes it to SiO_2. Moreover, these investigations show that the
silicon monoxide which forms during the Si+SiO_2 reaction, apparently,
differs in the construction of the polymeric chain, which tells not
only about the external form of the substance but also its chemical
activity. The values of apparent energies of activity were calculated
for the vitreous product (fig. 2, curve 3).

Silicon dioxide with chlorine can interact only at very high
temperatures. The introduction of a reducer into the system
significantly lowers the temperature of the chlorination of the
oxide.

For conducting the experiment we used optical quartz glass,
ground to 200 mesh, carbon electrode spectro-pure. The interaction of

silicon dioxide was studied at 300-1500°K.

The reactions of interaction $SiO_2 + Cl_2$ and $SiO_2 + C$ was not investigated in view of the fact that they occur at high temperatures which exceed the melting point of quartz glass from which the reaction flask is made. The information on the beginning of interaction SiO_2 with chlorine and carbon was taken from the literature. So, in [6] is it shown that silicon dioxide begins to interact with carbon at a temperature of 1800°K, and with chlorine at ~2000°C [7].

The interaction of SiO_2 with $SiCl_4$ in our conditions is impossible to realize since this reaction has a significant positive value of isobaric-isothermal potential.

The reaction of interaction of silicon dioxide with gaseous chlorine in the presence of a solid reducer begins at 1350°K, but occurs more intensely at 1500°K. The formed products of reaction (CO, CO_2, $SiCl_4$) are determined during heating repeated heatings (fig. 3). $SiCl_2$ is not found since in the studied temperature range and by thermodynamic calculations interactions (11) and (13) are not realized.

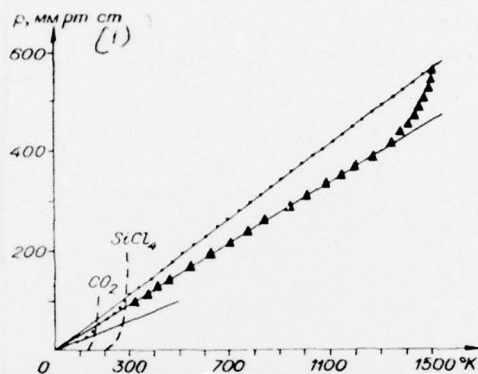From the given data it is obvious that the process of

Fig. 3. Tensiogram of interactions $SiO_2 + Cl_2 + C$.

Key: (1) mm mm Hg.

chlorination of SiO_2 in the presence of carbon occurs at lower
temperatures than the processes of interaction of dioxide with
chlorine and carbon. Having compared the thermodynamic calculations
and the experimental data on chlorination of silicon and its oxides,
and also having conducted an analogy with chlorination of germanium,
tin, and their oxides [1,2], we come to the conclusion that the
process of chlorination of the above oxides, including SiO_2, occurs
in several phases. The decrease of temperatures of chlorination with
the introduction into the system of a reducer is connected with the
chemosorption of chlorine on the active parts of the surface of the
oxide, which, weakening the bonds of metals - oxygen, facilitates the
passing of the reduction process. Even pure reduction can give the
possibility of realizing the process of chlorination in a specific
volume.

By the acquired tensiograms of the interactions of silicon and
its monoxide with chlorine, and also of silicon dioxide with chlorine
in the presence of carbon, the apparent energies of activation were
determined for non-isothermal processes by the equation presented in
[8]; we examined this question in more detail in [1,2]. For
interactions $Si+Cl_2$, $SiO+Cl_2$, SiO_2+Cl_2+C, the following values of
apparent energies of activation were found; 18, 39, and 65 kkal/mole,
respectively.

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